STUDY OF ELECTRICAL CONDUCTION MECHANISM OF POLYANILINE BENZOIC ACID BLEND PELLET

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Abstract - The electrical conduction mechanism of polyaniline-benzoic acid blend pellet has been studied at various temperatures in the range 313K to 353K. The results are presented in the form of I-V characteristics. Analysis has been made in the light of Poole-Frenkel, Fowler-Nordheim, Schottky, Ln(J) versus T plots, Richardson and Arrhenius plots. Results analysed suggest that, Schottky-Richardson mechanism is primarily responsible for observed conduction.

Keywords : Polyaniline benzoic acid blend pellet conductivity.

Introduction

A good amount of work has been reported on conduction mechanism in polymeric materials during past few years. Polymers are not simple covalent crystals of conventional solid state physics.[1] They exist as crystalline materials, as amorphous materials or as a mixture of crystalline and amorphous materials.

The electrical conduction in iodine doped polystyrene (PS) and polymethyl methacrylate (PMMA) has already been reported.[2,3] Japanese scientists have been particularly active in early research and development of these devices with work[4] on natural and synthesis polymers. Most of the early polymer electret work in US has been focused on using the polyelectric response for electromagnetic radiation detection.[5,6]

Burghate et al.[7] have reported the electrical conduction mechanism of succinic acid doped glycine pellet. The dc-conductivity of glycine was measured by Mishra et al.[8] to study the mechanism of electrical conduction. Belsare et al.[9] have reported the increase in electrical conductivity of polystyrene (PS) and polymethyl methacrylate (PMMA) with the increase in iodine doping concentration.

In the case of organic solids, whose conductivity due to electrons excited from valence band to conduction band[10,11] is negligible, a complex conduction behaviour[11,12] has been explained usually in terms of electron emission from cathode i.e. Schottky-Richardson mechanism[13] or by electron liberation from the traps in the bulk of the material i.e. Poole-Frankel mechanism.[14] The possibility of tunneling[15], space charge limited conduction[16] etc. have also been investigated in the literature.

In the present study, dc-conductivity of polyaniline-benzoic acid blend pellet was measured to identify the mechanism of electrical conduction. It is shown how the I-V data of the sample can be used to arrive at possible conclusions. Results have been discussed by plotting different mechanisms, such as Poole-Frenkel, Fowler-Nordheim, log(J) versus T plots, Schottky plots, Richardson plots and Arrhenius plots. In case of Schottky-Richardson mechanism, the current shows strong temperature dependence but not in case of Poole-Frenkel mechanism. The study of temperature dependence of current density is, therefore, of great importance.

Experimental Details

Preparation of samples

The conducting polymer polyaniline and benzoic acid (AR-grade) are used in the present investigation. The conducting polymer polyaniline was prepared in the laboratory by chemical oxidation method.[17] The mixture of 40% of polyaniline and 60% of benzoic acid, was prepared by using shell and mortar, and successively rubbing together for hours, so that a homogeneous mixture is obtained. This intimate mixture was poured in a pellet die, which was then subjected to a uniform pressure of

3 tonn/cm^2 using KBr press. The pressure was applied for three minutes. A fine uniform, shining pellet of the sample blend was obtained with perfectly smooth parallel faces. Both the surfaces of the pellet were coated with quick drying silver paint (supplied by Elteck Pvt. Ltd., Bangalore) to ensure good electrical contacts. The coated sample pellet was subjected to uniform heating at a temperature of 353K in furnace.

The x-ray powder diffractograph Fig 1 of sample has been recorded on Philips PW 1840 automated diffractograph at Department of Physics, Pune University, Pune. The Fig. 1 indicates that the crystalline structure appears in the diffractograph. The percentage crystalinity of the sample was calculated by Kaelble method[18] which has been found to be about 14.09%. The sample is therefore mostly amorphous.

Measurements

For the measurement of current and voltages, the thermostatically controlled furnace supplied by Tempo Industrial Corporation, Mumbai, was used for heating purpose. The mercury thermometer with an accuracy ± 1°C was used to record the temperatures. The regulated power supply supplied by Nuper India was used as the voltage source, while the current was recorded by using highly sensitive Pico-Ammeter (Model DPA III with accuracy ±0.2% supplied by Scientific Equipments, Roorkee). The sample pellet coated with silver electrodes was sandwiched between two brass-electrodes of the sample holder specially fabricated in the laboratory having electrode diameter of 2.4 cm each. This formed the metal-insulator-metal (M-I-M) system, which was placed in a furnace. The current (I) - voltage (V) measurements have been made at various constant temperatures from 313K to 353K.

Results and Discussion

The ln I - ln V plots of sample at various temperatures 313, 323, 333, 343 and 353K are shown in Fig. 2. The current increases nonlinearly with the applied voltage and does not follow a power law, I = kV^m, where k and m are constant.

The increase of current with voltage is rather weaker at low values of voltages and gets improved at higher voltages. Figure 2 indicates that (i) the current at a constant temperature increases with applied voltage (ii) the current at constant applied voltage increases with temperature. The mechanism operative in present case is discussed in the light of the Poole-Frenkel, Fowler-Nordheim, Schottky, ln(J) versus T plots, Richardson and Arrhenius plots.

Poole-Frenkel Mechanism

The current-voltage relationship for Poole-Frenkel mechanism[19] is expressed as,

$$J = Be^{\frac{-\phi}{kT} + \beta_{pf} E^{1/2}}$$

where $\square_{pf} = \square \frac{\square}{kT} \left(\frac{\square}{\square \in \in_0 d} \right)^{\square\square\square \, 1/2} = \text{constant}$ (1)

and predicts a field dependent conductivity as

$$\square = \square_0 \, e^{\frac{\beta_{pf} E^{1/2}}{2kT}} \qquad (2)$$

or

$$\log \square = \log \square_0 + \frac{\beta_{pf}}{2kT} E^{1/2}$$

(3)

so that the Poole-Frenkel mechanism is characterized by the linearity of $\ln\square$ versus $E^{1/2}$ plots i.e. Poole-Frenkel plots predicted by Eq. 3 are linear with a positive slope.

In the present case of polyaniline benzoic acid blend pellet the ln□ versus $E^{1/2}$ plots are linear but with a -ve slope (Fig. 3) indicating the absence of PF mechanism.

Fowler-Nordheim Mechanism

The Fowler-Nordheim relation[20] for current density is

$$J = AV^2 e^{\frac{-\phi}{V}}$$

so that, $\ln \frac{J}{V^2} \quad = \ln \ A \frac{\phi}{V} \ (\quad)$

And the $\ln \frac{J}{V^2}$ versus I/V plot is expected to be linear straight line with a -ve slope.

In this case the $\ln \frac{J}{V^2}$ versus I/V plot for the sample is presented in Fig. 4 which are nearly straight line with a +ve slope higher as well as lower value of V (and of course E) indicating the absence of F-N mechanisum.

Schottky plots

Thermal activation of electron, may occur over the metal insulator interface barrier, which is further helped by the applied electric field effect, which reduces the height of the barrier. The Schottky-Richardson current voltage relationship is expressed as:

$$J = AT^2 e^{\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}}$$

$\square_{SR}$ being the field lowering constant given by

$$\square_{SR} = \square \frac{e}{kT} \left(\frac{e}{4\square \in \in_0 d} \right)^{1/2} \square \square \square$$

and hence

$$\frac{\phi_s}{kT} + \beta_{SR} E^{1/2}$$

$\ln J = \ln AT^{2}$ and that $\overline{\ln}$ J versus $\sqrt{E}$ plot should be a straight line with a +ve slope.

Schottky plots for the present case are shown in Fig. 5. The relation expects a +ve slope, which is observed in the present case, and as such indicates the applicability of the mechanism. Further, in case of Schottky-Richardson mechanism the current shows strong-temperature dependence but not in case of Poole-Frenkel mechanism. The study of temperature dependence of current density is, therefore, of great importance.

Current density versus temperature plots

The temperature dependence of current density is presented in the form of ln J versus T plots in Fig. 6, and that the increment in current due to rise of temperature is quite appreciable. The strong temperature dependence is suggestive of Schottky-Richardson mechanism, which is observed in this case.

Richardson mechanism

The Richardson current voltage relationship is expressed as,

$$J = AT^2 e^{\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}}$$

$$\frac{J}{T^2} = A e^{\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2}}$$

$$\log \frac{J}{T^2} = \log A + \left(\frac{-\phi_s}{kT} + \beta_{SR} E^{1/2} \right)$$

$$\log \frac{J}{T^2} = \log A + \square_{SR} E^{1/2} \frac{\phi_s}{kT}$$

The graph between J/T^2 versus 1/kT plots from this relation should be a straight line with a negative slope.

In the present case straight line graphs have been obtained with a -ve slope. The linearity of the plots support Schottky-Richardson mechanism (Fig. 7).

Arrhenius plots

The ln □ versus 1/T plots (Fig. 8) at all values of applied voltages show straight line with -ve slope. This enables us to calculate the activation energy for conduction which has been found out to be 0.12 eV. This is in good agreement with the reported order of magnitudes.

Conclusion

S-R mechanism of conduction predominates over other mechanisms in the sample. The applied field value seems to be insufficient to liberate electron from traps, showing absence of PF mechanism. Even though the electric field value and the temperature range is lower to activate contribution from other mechanism, yet the activation energy can safely be calculated and is found to be well within range for similar samples.

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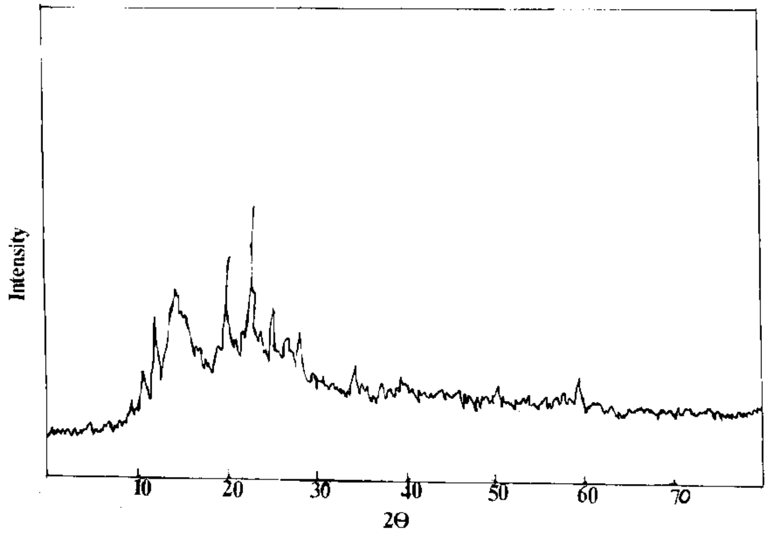


Fig 1 X-ray diffractogram of sample

Fig 2 : Current Voltage Characteristics

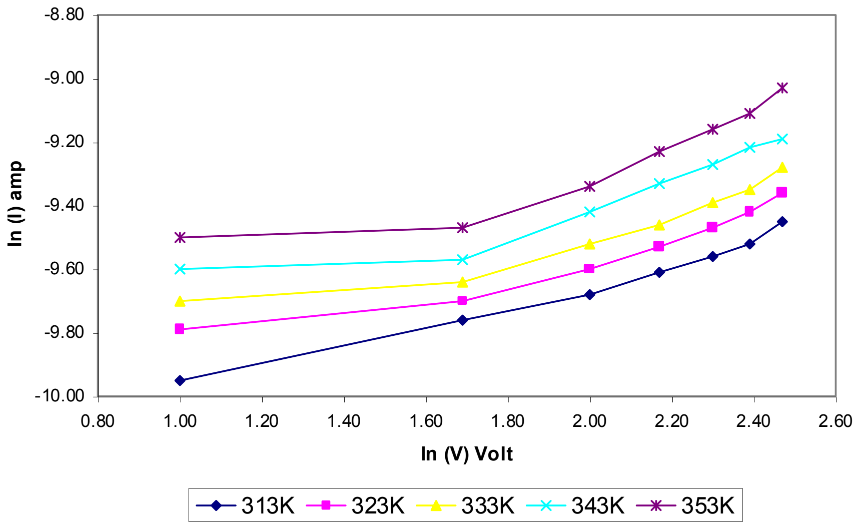


Fig 3 : Poole Frenkel Plots

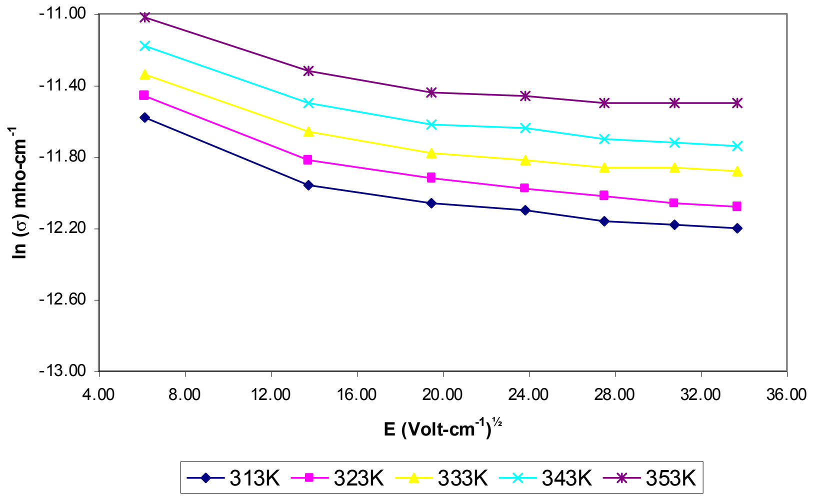


Fig 4 : Fowler-Nordheim Plots

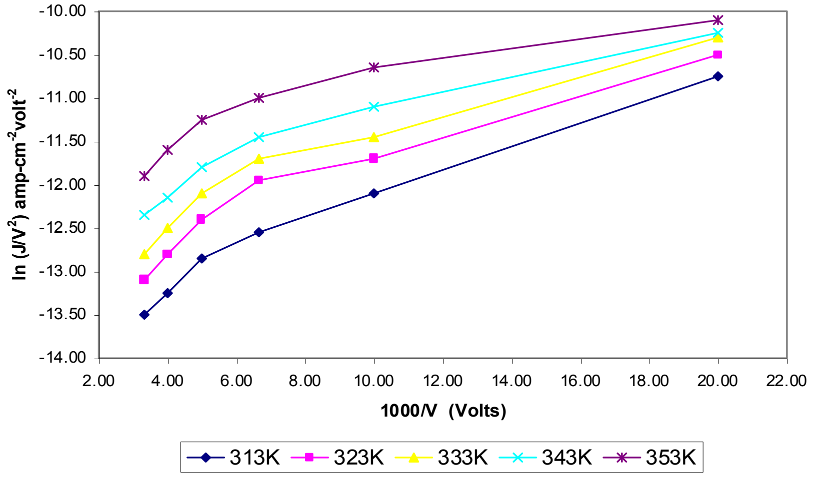


Fig 5 : Schottky Plots

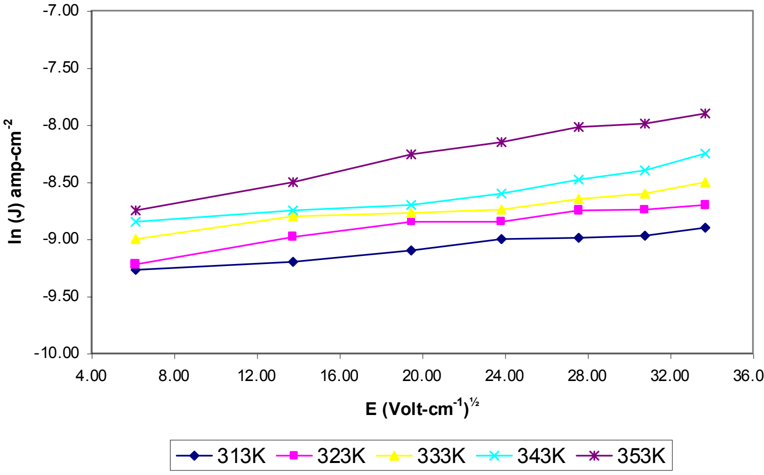


Fig 6 : Current Density versus Temperature Plots

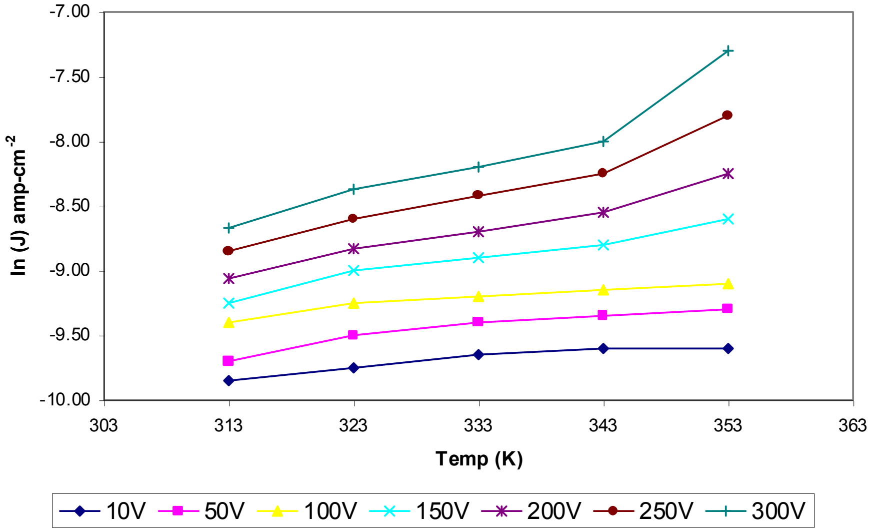


Fig 7 : Richardson Plots

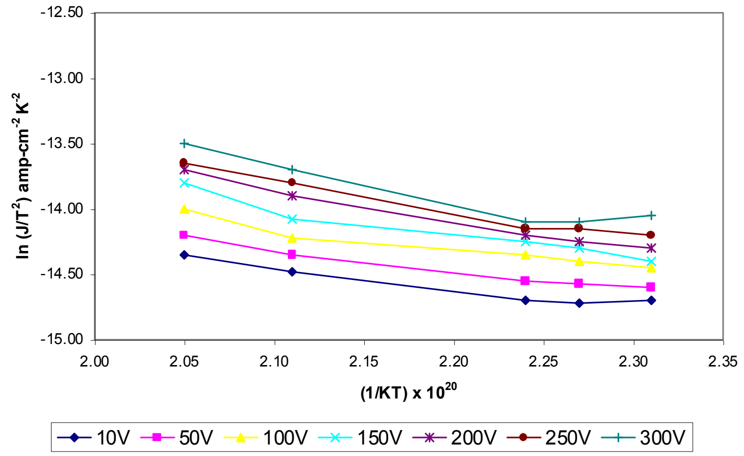
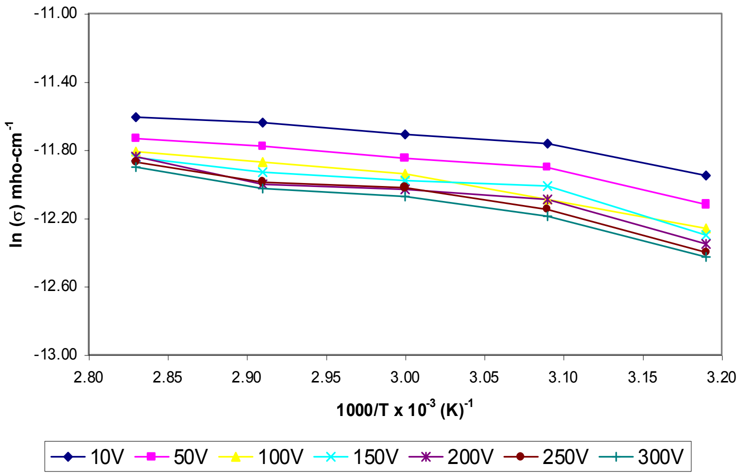


Fig 8 : Arrhenius Plots



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